Spectroscopic signatures of a bandwidth-controlled Mott transition at the surface of *1T*-$TaSe_2$

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High-resolution angle-resolved photoemission (ARPES) data show that a metal-insulator Mott transition occurs at the surface of the quasi-two dimensional compound $1T$-$TaSe_2$. The transition is driven by the narrowing of the Ta *5d* band induced by a temperature-dependent modulation of the atomic positions. A dynamical mean-field theory calculation of the spectral function of the half-filled Hubbard model captures the main qualitative feature of the data, namely the rapid transfer of spectral weight from the observed quasiparticle peak at the Fermi surface to the Hubbard bands, as the correlation gap opens up.

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Electronic correlations can modify the electronic structure of solids not only quantitatively, but also qualitatively, inducing new broken-symmetry phases which exhibit charge, spin or orbital-order, and more exotic states in low dimensions. One of the most notable consequences of electronic correlations is the much studied metal-insulator (M-I) Mott transition [1, 2]. Recently, new theoretical approaches have considerably extended our understanding of this fundamental problem [2, 3].

Many physical properties indirectly reflect the dramatic rearrangement of the electronic structure at the transition. Photoelectron spectroscopy, which probes the single-particle spectral function, can provide a direct view of such changes [4, 5, 6]. However, comparing samples with different compositions faces materials problems like stoichiometry, defects, and disorder. A quantitative analysis is further complicated by the known surface sensitivity of the technique [7][8]. An ideal experiment would record the energy and momentum-dependent spectrum, while tuning the crucial (W/U) parameter (U is the on-site Coulomb correlation energy; W is the bandwidth) *in the same single crystal sample*. Remarkably, it is possible to approach this ideal situation exploiting the occurrence of modulated structures (charge-density-waves; CDWs) in appropriate low-dimensional systems. There, the lattice distortion modulates the transfer integrals and therefore modifies the bandwidth. In materials that are close enough to a Mott transition, the reduced bandwidth may lead to an instability. There are strong indications for this scenario in the layered chalcogenide $1T$-TaS_2, which presents a sharp order-of-magnitude increase of the resistivity at T=180 K [9, 10], with a strong rearrangement of the electronic states [11, 12, 13, 14, 15]. However, the complex phase diagram of the CDW in $1T$-TaS_2 affects the electronic transition, which cannot be considered as a typical Mott transition.

Isostructural and isoelectronic $1T$-$TaSe_2$ exhibits a similar CDW, but only one phase below T_C=475 K. Its electrical resistivity remains metallic - albeit rather large - to very low temperatures [9], suggesting that the Se compound lies further from the instability than the S analog. Nevertheless, a transition could still occur at the crystal surface, where the U/W ratio is expected to be larger as a result of smaller screening and coordination. The surface sensitivity of ARPES is ideal to investigate such an inhomogeneous state. In this Letter we present evidence for a Mott transition at the surface of $1T$-$TaSe_2$. High-resolution temperature-dependent ARPES shows for the first time the disappearance of the coherent quasiparticle signatures at the Fermi surface and the opening of a correlation gap. These results are qualitatively well described by a dynamical mean-field (DMFT) calculation, and provide new insight into the spectral properties of the MI transition.

$1T$-$TaSe_2$ has a layered structure, with the d^1 Ta atoms in a distorted octahedral environment. Adjacent layers interact weakly through van der Waals gaps, and all physical properties exhibit a strong anisotropy. A threefold CDW develops below $T_C = 475K$, with a commensurate $\sqrt{13} \times \sqrt{13}$ superstructure, analogous to the much studied low-temperature CDW phase of $1T$-TaS_2[9]. In real space the CDW corresponds to a modulation of the atomic positions, within a 13 Ta atoms unit, in the so-called 'star-of-David' configuration. Extended Huckel calculations [16] suggest that the CDW splits the Ta d conduction band into subbands which contain a total of 13 electrons per unit cell. Two subbands, carrying 6 electrons each, are filled and lie below the Fermi level.

The Fermi surface is formed by a half-filled subband carrying the 13th electron. The opening of a correlation gap in this subband is responsible for the resistivity jump in (bulk) $1T$-TaS_2[10].

We performed high-resolution ARPES measurements in Lausanne and at the PGM beamline of the SRC, University of Wisconsin. The energy and momentum resolution were ΔE=10 meV and $\Delta k = \pm 0.02 \text{Å}^{-1}$, and the Fermi level location was determined with an accuracy of $\pm$ 1 meV by measuring the metallic edge of a polycrystalline gold reference. Single crystal samples grown by the usual iodine transport technique were characterized by Laue diffraction and resistivity measurements, which confirmed the assignment to the *1T* polytype. They were mounted on the tip of a closed-cycle refrigerator and cleaved at a base pressure of 1×10^{-10} torr. We did not observe any sign of surface degradation or contamination over a typical 8 hours run.

Figure 1 shows ARPES intensity maps (hν = 21 eV) measured at 300 K and 70 K along the high-symmetry ΓM direction of the hexagonal Brillouin zone (BZ). A higher photon energy (hν = 50 eV) yields similar results. The maps correspond to the same CDW phase, as confirmed by low-energy electron diffraction (LEED), but exhibit remarkable differences. At 300 K the narrow topmost Ta d subband crosses the Fermi level at $k_{F_{1,2}} \sim \pm$ 1/4 ΓM, in good agreement with band structure calculations [17]. The filled CDW subbands are visible at $\sim$ 0.3 eV and, with lower intensity at larger binding energies ($\sim$ 0.8 eV) and momenta. The overall dispersion of the Ta d band is influenced by the CDW superlattice, as will be discussed elsewhere. The parabolic band with a maximum at Γ and $\sim$0.5 eV is a Se p band. At 70 K the Ta d spectral weight is narrower and clearly removed from E_F, and a gap has appeared.

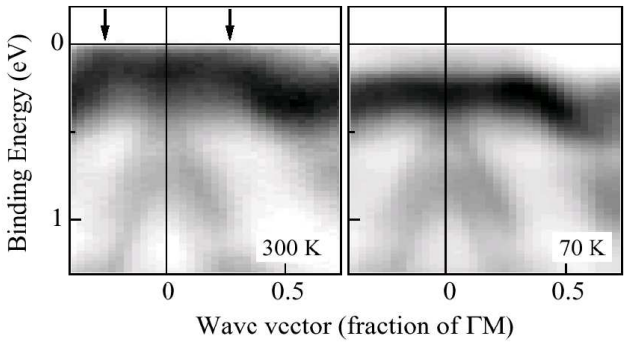

FIG. 1: ARPES intensity maps of $1T$-$TaSe_2$ at T=300 K (left) and T=70 K (right) measured along the ΓM high-symmetry direction (hν=21 eV). The arrows mark Fermi level crossings by the Ta 'd' band at 300 K.

Bulk sensitive properties and surface sensitive LEED data rule out a structural phase transition between 300 K and 70 K. The large spectral changes are therefore the consequence of an electronic surface transition. Signatures of a surface gap in $1T$-$TaSe_2$ were previously observed at 70 K by scanning tunneling spectroscopy (STS) [18]. We characterized this transition by temperature-dependent measurements of the shallow Ta $4f$ core levels, which exhibit a CDW-induced fine structure [11, 19]. We find (not shown) that between 300 K and 70 K the CDW-split components sharpen, and their energy separation increases by 40 meV, in agreement with lower-resolution data [20]. We conclude that the CDW amplitude and the corresponding lattice distortion are larger at the lower temperature.

The increased distortion reduces the overlap between the 'cluster orbitals' which form the basis of the band structure in the CDW phase. Calculations which explicitely account for this effect are not available, but the (W/U) ratio is certainly reduced, possibly below the critical value for the M-I transition. This is confirmed by an inspection of the ARPES signal at $k = k_{F_1}$ (Fig. 2a), which reveals a sudden loss of intensity near E_F below $\sim$260 K, and the appearence of a strong signal centered at 0.26 eV. All spectra were normalized to the same integrated area. The intensity at E_F (Fig. 2b) exhibits a sharp step around 260 K, and a further linear decrease at lower temperature. The intensity and the spectral lineshape (not shown) are recovered upon heating, but only at higher temperatures. The large hysteresis ($\sim$ 80K) suggests a first-order transition [21].

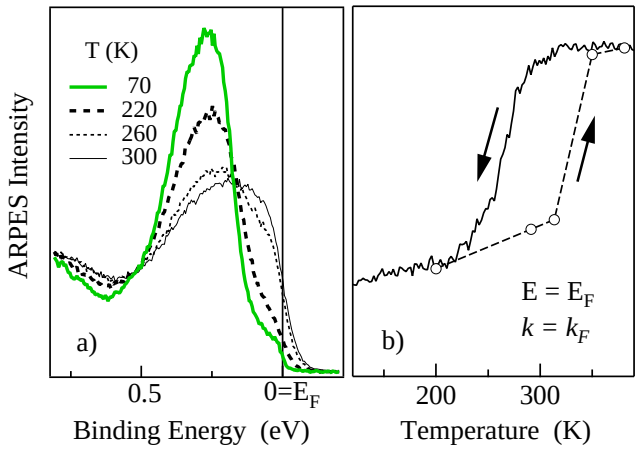

FIG. 2: a) ARPES spectra measured at $k = k_{F_1}$ between 300 K and 70 K; b) Temperature dependence of the ARPES signal at the Fermi surface, showing a sharp break, and a large hysteresis.

In Fig. 3, following common practice in ARPES work on the cuprates, we symmetrized the spectra of Fig. 2a around E_F. This procedure removes the perturbing effect of the Fermi distribution on the intrinsic temperature dependence of the spectral function $A(k_F, \omega, T)$. The 300 K spectrum exhibits a broad ($\sim$1 eV) incoherent background and a weak quasiparticle (QP) feature at E_F. The QP signal disappears at lower tempera-

ture, and spectral weight is transferred to the lower and - as inferred by symmetry - upper sidebands, representing the lower (LHB) and upper (UHB) Hubbard subbands. The integrated intensity is conserved. We emphasize that the width (∼100 meV) of the central peak is much larger than expected for a coherent quasi-particle at the Fermi surface of a 'good' metal. Clearly, in the 220-260 K temperature range, the corresponding excitations are heavily scattered, and their lifetime is short. This 'bad metal' character is consistent with the broad maximum and large value of the electrical resistivity of bulk $1T$-$TaSe_2$ at 250-300 K [9].

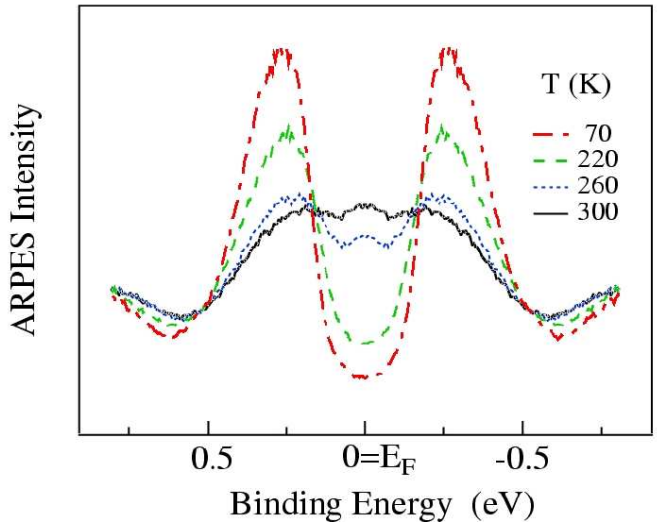

FIG. 3: Temperature-dependent ARPES spectral function at $k = k_{F_1}$ (hν=21 eV). The spectra have been obtained from the raw spectra I(E) by symmetrization around E_F: I*(E)=I(E)+I(-E).

The spectra of Fig. 3 are qualitatively consistent with the changes expected at the Mott transition. In order to substantiate this, we have calculated $A(k_F, \omega; T)$ for a one-band Hubbard model at half-filling, within the dynamical mean-field theory (DMFT) framework [3]. The "iterated perturbation theory" approximation [22] was used, and checks were made using Quantum Monte Carlo and the maximum entropy method. The Coulomb term U was set at 0.52 eV, equal to the energy separation between the LHB and UHB features in Fig. 3. A semicircular density of states was used, with a bandwith W assumed to depend linearly on temperature between 300 K (W=0.50 eV) and 70 K (W=0.36 eV). These values are only indicative, and are not the result of a specific attempt to find an optimum fit to the data, but we note that the overall magnitude of W is consistent with the dispersions observed in Fig.1.

The high-temperature (300 K, 260 K) calculated spectra (Fig. 4) correspond to a correlated metal in the incoherent regime, with a broad low-energy peak and two intense Hubbard sidebands. The central peak is strongly reduced at 220 K, and at 70 K it has disappeared completely, leaving two sharp features centered at $\pm U/2$ and separated by a real gap. The overall shape of the spectra is in good qualitative agreement with the data, as well as the dramatic transfer of spectral weight that takes place between the central peak and the Hubbard bands as the temperature is lowered. We observe that in both theory and experiment the spectral weight accumulated in the insulator near the maximum of the HB sidebands comes mainly from the QP central peak, but that a small fraction also comes from energies above 0.5 eV. This results in two energies at which all spectra approximately cross. The data provide the first direct momentum-resolved observation of two of the key predictions of DMFT regarding the one-particle spectrum through the Mott transition, namely the three-peak structure in the metallic state [22] and the large transfers of spectral weight from the metal to the insulator [23, 24, 25]

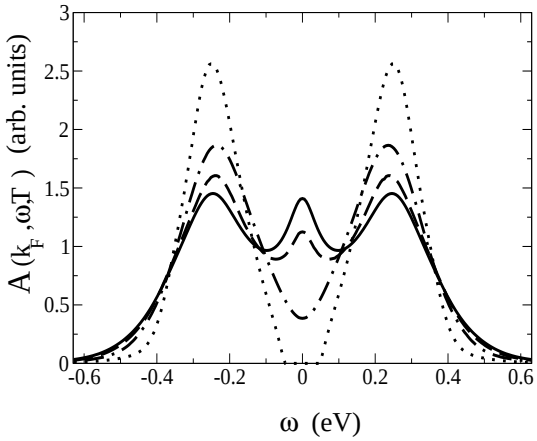

FIG. 4: Temperature-dependent spectral function $A(k_F, \omega)$ of the half-filled Hubbard model calculated within DMFT for the temperatures of Fig. 4. U was fixed at U=0.52 eV, and the bandwidth is chosen as: W=0.50 eV at 300 K (solid); 0.48 eV at 260K (dash); 0.44 eV at 220K (dash-dot); and 0.36 eV at 70 K (dot).

The comparison of theory and experiment also reveals some differences. Unlike the calculated spectra, the intensity at E_F is never completely suppressed in the experimental spectra. This signal could originate from the underlying metallic bulk, or from surface inhomogeneities (metallic 'patches') observed by STS [18]. It could also indicate that the tails of the LHB and UHB overlap slightly, a passibility which was considered in a different context [26]. Another quantitative difference is the sharper separation between the QP peak and Hubbard bands in the calculation. This is a known feature of DMFT which is likely to be weakened as dimensionality is lowered. Recent work in particular [27] suggests that long-wavelength charge modes partially fill the preformed gap.

From a theoretical standpoint, the main discrepancy concerns the value of the critical temperature at which

the first-order metal insulator transition is observed. Indeed, with the observed value of U, the simple one-band Hubbard model treated within DMFT would have a first-order transition at T$\simeq U/80 \simeq$ 90 K, a factor of three smaller than observed experimentally. The trajectory in the (T,(W/U)) space used in the theoretical calculation does not intersect the first-order transition line, so that theory would interpret the spectral changes as due to a rapid crossover between a bad metal and a Mott insulator. On the other hand the experimental observation of a hysteresis does suggest a real transition. In a purely electronic model, it is known that orbital degeneracy does lead to increased T_c values [28]. However, DMFT model calculations including the whole d manifold, show a significant increase in T_c only when the first subband is much closer to the Fermi level than in the experiment. Thus, it is unlikely that orbital degeneracy could explain the increased T_c. The inadequacy of a purely electronic model is also suggested by the large width of the low-energy QP. In a purely electronic model, this can only be accounted for if the temperature is significantly larger than the critical temperature for the metal-insulator transition.

The observation of a broad peak and a true transition strongly suggests that the coupling to lattice degrees of freedom plays an important role, as in fact expected in a CDW compound. Indeed, it has been shown in a simple model that the coupling to the lattice can lead to an increase in T_C [29]. Also, it is possible that the observed hysteresis results from differences in the pinning of the CDW upon heating and cooling. Obviously, further investigation - both theoretical and experimental - is required to clarify these issues.

In summary, we presented momentum-resolved high-resolution ARPES data which illustrate the spectral consequences of a bandwidth-controlled surface Mott transition in $1T$-$TaSe_2$. The transition from a bad-metal, characterized by a largely incoherent spectrum, to a correlated insulator is qualitatively captured by a DMFT calculation for the half-filled Hubbard model. Quantitative differences between theory and experiment suggest that the model should be extended to include the coupling to lattice degrees of freedom, in order to provide a more accurate description of electronic transitions in such CDW materials.

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